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PROCESSES OF DIELECTRIC AND NMR RELAXATION IN THE
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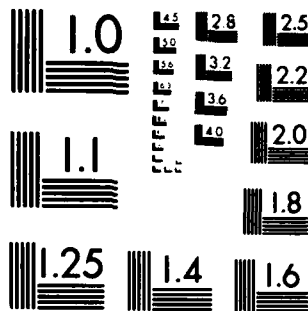
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PROCESSES OF DIELECTRIC AND NMR RELAXATION IN THE SURFACE LAYERS
OF ACRYLATE - EPOXY - STYRENE COMPOUNDS

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(from Russian)

At the present time in addition to hot-setting epoxy resins cold-setting resins are also acquiring great importance. As a rule, aliphatic amines - hexamethylene-diamine, polyethylenepolyamine etc - are used as curing agents for these resins. The compounds obtained in this case, however, are very viscous, have low impregnating capacity and are not technologically satisfactory in service. Their setting involves the use of toxic curing agents, and the cured compounds do not have very high physico-chemical or mechanical indices (Refs 1 - 3).

Epoxy-polyester resins into which anhydrides of dicarbonic acids have been introduced may also be used as cold-setting compounds, though high indices in these compounds are achieved by high-temperature processing (Ref 4).

Of considerable interest are cold-setting acrylate-epoxy-styrene compounds (Ref 5) which have satisfactory technological characteristics in service and do not require toxic curing agents. As these compounds are used to produce filled polymers it is worth examining the behaviour of the boundary layers of acrylate-epoxy-styrene compounds on different solid surfaces depending on the nature of the initial components.

In the present investigation we studied the molecular mobility of the polymer chains of various acrylate-epoxy-styrene compounds depending on the nature of the initial components, and also elucidated the nature of changes of molecular mobility in the boundary layers on surfaces of silica flour and glass fibre to assess their effect on the properties of filled materials. As the cured compounds under investigation contained different amounts of low-molecular impurities (water, unreacted initial monomers) depending on the acrylate component, we elucidated the effect of low-molecular impurities on the course of the relaxation processes in the surface layers on different types of surfaces.

Specimens and Method of Measurement

We studied the dielectric and spin-lattice relaxation of cold-setting acrylate-

epoxy-styrene compounds in bulk and in the surface layers on surfaces of silica flour and glass fabric. One of the features of this compound is that the curing agent employed is a copolymer of methacrylic (acrylic) acid, styrene and methylmethacrylate (methylacrylate, butylacrylate) obtained in the presence of a redox system of benzoyl peroxide and dimethylaniline. The copolymer is formed in the reaction mixture containing all the initial components in the first stage (refs 5, 6), and this is followed by the reaction in which a cross-linked polymer is formed by opening of the epoxy groups. The copolymer contains sufficient carboxyl groups to cure the epoxy resin, this reaction being catalysed by the dimethylaniline and promoted by the exothermic reaction of copolymer formation.

The following compounds were investigated:

1. Resin ED-6 : styrene : methylmethacrylate : methacrylic acid = 4:3:2:1
2. Resin ED-6 : styrene : butylacrylate : acrylic acid = 4:3:2:0.8
3. Resin ED-6 : styrene : methylacrylate : acrylic acid = 4:3:2:0.8.

All the initial monomers were subjected to distillation and checked for n_D on a refractometer. The reinforcing glass fabric was degreased with toluene. The silica flour and glass fabric were heated in a muffle furnace at 400°C for 0.5 h, after which they were vacuum-dried at 110°C for 6 h. To prevent the fillers from absorbing moisture from the environment, they were kept after vacuum drying in a vacuum in a vacuum-drying cabinet until they were fully cooled, and filling of the specimens was carried out in this. The dry fillers were coated with freshly prepared reaction mixture which has a very low viscosity, as the styrene and methylmethacrylate (methylacrylate, butylacrylate) were at the same time both initial monomers of the compounds produced and reactive solvents. After careful mixing of the silica flour (particle size 20 - 40 μ m) and the reaction mixture, and impregnation of the glass fabric with the reaction mixture, setting was carried out in condenser cells made of stainless steel. The specimens for NMR measurements were cured in closed ampoules. Films were poured on a lavsan (terylene) substrate. With all these specimens of acrylate-epoxy-styrene compounds the cross-linking reaction was carried out in an air-free environment. Measurements were carried out in a vacuum. The ratios of the components for compound:silica

flour and glass fabric:compound were 1:1.5 and 1:1 respectively. The filled and unfilled specimens of each compound were prepared with the same reaction mixture. The spin-lattice relaxation times were measured by the Carr-Purcell zero method using a pulse spectrometer operating on a frequency of 16.5 MHz. We used an NMR spectrometer type RYa 2301 modified for pulse method operation. Dielectric measurements were made with a TR-9701 instrument using an F-550 zero indicator and a VM-544 generator in the temperature interval -150 to +130°C.

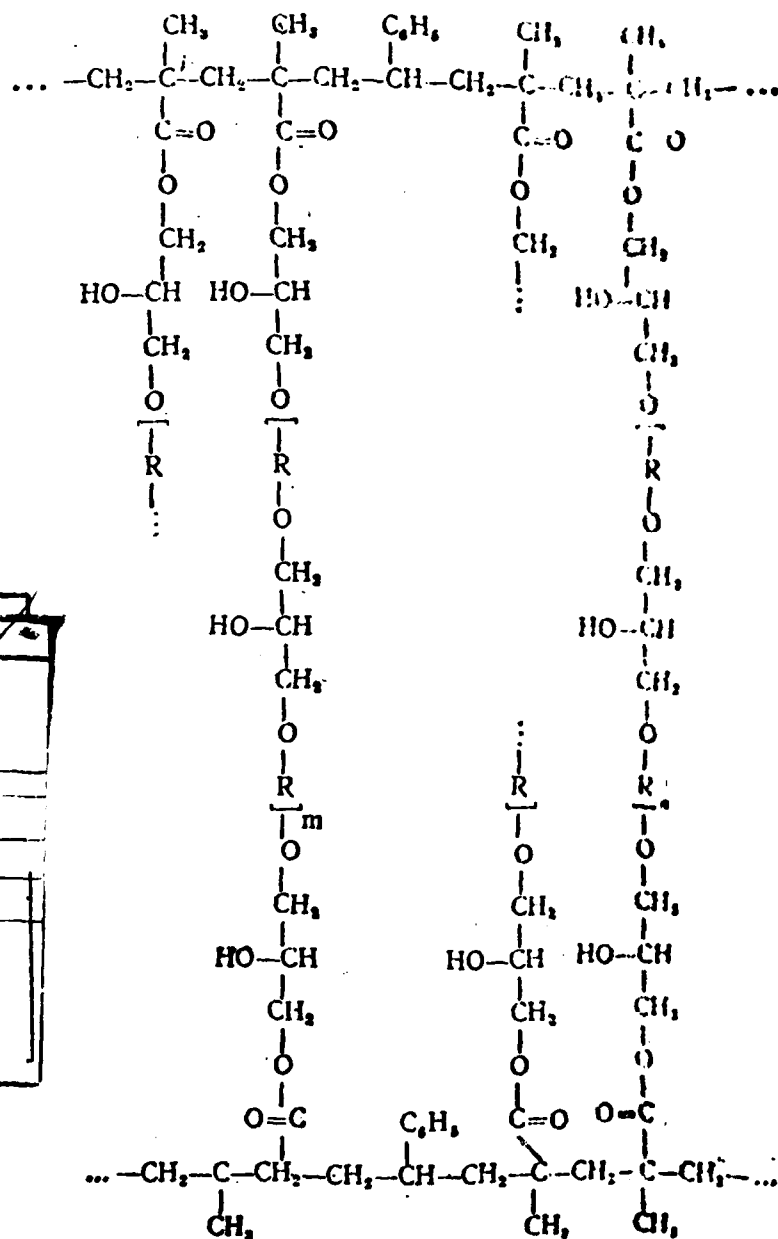
Results and Discussion

1. Relaxation Processes in Bulk

As may be seen from the temperature dependences of $\tan \delta$ (Fig 1) three relaxation processes are characteristic of the compounds examined in bulk: a process due to chain segment mobility in the region of 60 - 90°C; a dipole-group process at -140 to 145°C; and a process at -50 ÷ 40°C due to the mobility of units (parts of chains and their branches) smaller than segments and larger than the kinetic units producing the dipole-group process.

Consideration of the high-temperature relaxation process shows that substitution of the acrylic components in the systems leads to noticeable changes in molecular mobility and in the absolute value of $\tan \delta$ at the maximum. The lowest molecular mobility is found in the system containing methylacrylate and acrylic acid (Fig 1, curve 3). When butylacrylate is used instead of methylacrylate the mobility of the chain segments of the compound increases, with a shift of the maximum of $\tan \delta$ to higher temperatures amounting to 11°. For compounds based on methylmethacrylate and methacrylic acid segmental mobility is somewhat greater (Fig 1, curve 1), and as the amount of dimethylaniline is reduced the $\tan \delta$ maximum shifts to lower temperatures (curves 4, 1), which may be accounted for by a lower degree of cross linking in the system. Fig 1 shows that compounds based on butylacrylate and methylacrylate have values of $\tan \delta$ at the maximum greater by one order (curves 3, 2). Special attention should be drawn to the fact that, for the cold-setting acrylate-epoxy-styrene compounds we studied, the high-temperature relaxation process is very distinct and is associated with a high amplitude of the $\tan \delta$ maximum. This is not observed in cross-linked systems based on epoxy resins and

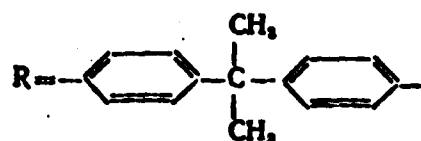
polyethylenepolyamine. The occurrence of clearly marked maxima of high value is explained by the fact that the process of relaxation of the segments is mainly due to the existence of parts of chains of the styrene/acrylate/acrylic acid copolymer cross-linked in a spatial structure by chains of epoxy resin. This can be seen from a fragment of the compound



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The results of studies of the molecular mobility of acrylate-epoxy-styrene compounds using dielectric measurements are corroborated by results obtained from spin-lattice relaxation times T_1 (Fig 2, a).

II. Molecular Mobility of Macrochains in the Surface Layers.

Studies of the molecular mobility in the surface layers of acrylate-epoxy-styrene cold-setting compounds showed that changes in relaxation processes in the boundary layers are independent of the nature of the surface (Refs 7 - 9). Furthermore, the findings described below also show that there is rigidification of the polymer chains due to adsorptive interaction and reduction of the conformation set of polymer chains at the surface, and also that the presence of low-molecular impurities has a significant effect on changes in the properties of the polymer in the surface layer.

Fig 3, a shows that on the surface of the glass fabric and the silica flour there is a shift of the relaxation process of the chain segments of the compound containing methylmethacrylate and methacrylic acid to higher temperatures, amounting to 18° at the surface of silica flour, and 9° at the surface of the glass fabric. We account for the significantly smaller shifts on the surface of the glass fabric filler by the fact that the percentage of glass fabric used as a filler is significantly lower than that of silica flour (the glass fabric : compound ratio was 1:1, whereas the silica flour : compound ratio was 1.5:1), i.e. the thickness of the surface layer of the polymer on the glass fabric is greater than it is on the silica flour. In other words, the total surface of interaction between silica flour and polymer is greater than the total contact surface between glass fabric and polymer.

A principal factor affecting the reduction of the temperature shifts of the $\tan \delta$

maximum in the surface layer at the surface of the glass fibre filler in this case is the fact that in the surface layer on the surface of the silica flour the amount of low-molecular impurities is about 0.5 times lower than in the surface layer on the glass fabric surface. The amount of low-molecular impurities in the acrylate-epoxy-styrene compounds in bulk and in the surface layers was determined by weighing after vacuum treatment for 10 hours at room temperature and for 9 hours at 68°C (vacuum of $2 \cdot 10^{-2}$).

For the same system based on methylmethacrylate and methacrylic acid the dipole-group process shifts to lower temperatures by 28° on the silica flour surface, and by 24° on the surface of the glass fabric filler. We associate the shift of this process to lower temperatures with increased looseness of packing in the surface layer in accordance with refs 7 - 10. With increase of the low-molecular impurities in the specimens (unreacted initial monomers, water etc), which was observed in the compound based on butylacrylate and acrylic acid (Fig 3, b), the shift of the $\tan \delta$ maximum to higher temperatures was considerably smaller (8°), and on the surface of the glass fabric filler it was seen to be split up with relatively symmetrical peaks shifted in opposite directions equal distances about the $\tan \delta$ maximum in bulk.

In the compound based on methylacrylate and acrylic acid the amount of low-molecular impurities was even larger (up to 1.5% when determined without heating, and 4.8% with heating, see Table), which led to a shift of the relaxation process of chain segments to lower temperatures on the surface of the glass fabric. In the layer on the surface of the silica flour the shift to higher temperatures only amounts to 6° (Fig 3, b).

From the above findings it follows that changes of molecular mobility in the surface layers are significantly influenced by the presence of low-molecular impurities in the systems studied, and also by the tendency of the filler to adsorb them. Low-molecular impurities exert a plasticising effect on the polymer at the surface and shift the relaxation process to lower temperatures, thus reducing the effect of rigidification of the chains by the surface, or even totally offsetting it. As silica flour adsorbs low-molecular impurities more than

glass fabric, in all cases (Fig 3) as their content in the systems studied is increased, the shift to higher temperatures is decreased. In the glass fabric the greater amount of impurities in the boundary layer leads not only to a smaller shift to higher temperatures because of the effect of the surface, but also to shifts to lower temperatures (Fig 3, b). The influence of impurities on the course of the relaxation processes can also be seen from data on spin-lattice relaxation times T_1 (Fig 2).

The splitting of the $\tan \delta$ maximum which we detected in the relaxation process of chain segments for filled polymers (Fig 3, b) is also observed in the compound with methylmethacrylate and methacrylic acid (Fig 3, a), where in the ratio of the components of the reaction mixture 0.01 parts of dimethylaniline are taken instead of 0.03. This splitting of the maximum would seem to be due to inhomogeneity of the structure of the boundary layer near the surface and a short distance away from it, but more detailed investigations are needed to find the true reasons for it.

As the increase of low-molecular impurities is not so noticeable in the system with a smaller amount of dimethylaniline (see Table), it may be supposed that oligomer molecules of small molecular weight are formed which are not removed by vacuum treatment and which act as a plasticiser for the polymer matrix, so that with this compound we do not observe upward temperature shifts of the relaxation process of the segments at the surface of the solid (Fig 3, a).

The change of molecular mobility in the surface layers to a great extent depends on the presence of low-molecular impurities in the systems studied. The nature of the surface of the filler affects the magnitude of the excess over the maximum amount of low-molecular impurities which can be adsorbed by the solid surface, i.e. they become concentrated at the surface of the solid due to adsorption primarily at the interface. Low-molecular impurities which are capable of exerting a plasticising effect shift the relaxation processes to lower temperatures, thereby partially or totally offsetting the effect of the filler surface.

III. Relaxation Processes in Heat-treated Compounds

We carried out studies of molecular mobility in heat-treated compounds. The heat

treatment of specimens for dielectric measurements involved heating steadily from 20 to 130°C for 5 hours with maintenance at this temperature for 10 minutes.

Specimens for NMR measurements were heat-treated to 200°C in a similar way.

Figs 2, a and 3, a show the temperature dependences of T_1 and $\tan \delta$ for compounds containing methylmethacrylate and methacrylic acid, and indicate that heat treatment shifts the relaxation process to higher temperatures, the shifts amounting to 40 - 50°. Here the values of $\tan \delta$ are not significantly reduced. This is associated with the process of cross linking at deeper stages involving -OH groups and possibly unreacted -COOH groups.

The study of filled systems has shown that in a heat-treated, more rigid, compound the shift of the $\tan \delta$ maximum in the surface layer is reduced (being 12°), whilst in a non-heat-treated one the shift is 21°. This supports our conclusions that for a more flexible polymer constraint of molecular mobility by the surface is greater (Ref 11) than it is with more rigid macrochains.

Conclusions

1. A study has been made of the dielectric and spin-lattice relaxation of cold-setting acrylate-epoxy-styrene compounds. The existence of three relaxation processes has been demonstrated.
2. It has been found that for acrylate-epoxy-styrene compounds rigidification of the polymer chains in the surface layer occurs on surfaces of various kinds.
3. Changes of molecular mobility in the surface layers depend to a great extent on the presence of low-molecular impurities in the surface layer. A low-molecular impurity capable of exerting a plasticising effect shifts the relaxation processes to lower temperatures, partially or totally offsetting the effect of the substrate on molecular mobility.
4. Studies of heat-treated filled systems have shown that with increasing chain rigidity the magnitude of the constraint exerted by a solid substrate on molecular mobility diminishes, i.e. the more rigid the macromolecules, the less they are rigidified by the surface of the filler.

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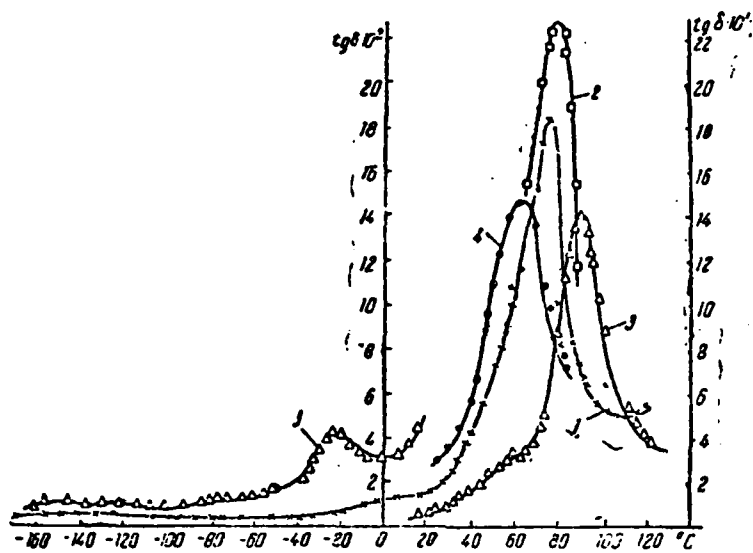


Fig 1. Temperature dependences of $\tan \delta$ in compounds based on:

1 - styrene, methylmethacrylate, methacrylic acid and ED-6; 2 - styrene, butyl acrylate, acrylic acid and ED-6; 3 - styrene, methylacrylate, acrylic acid and ED-6; 4 - styrene, methylmethacrylate, methacrylic acid, ED-6 and with 0.01 part by weight of dimethylaniline instead of 0.03 (as used in compounds 1 - 3).

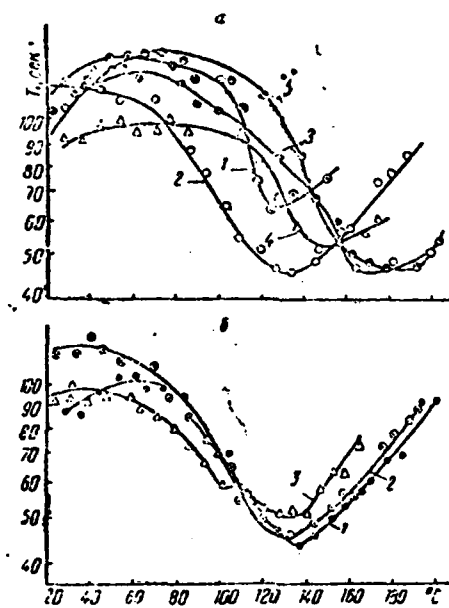


Fig 2. Temperature dependences of T_1 :

a) for compounds containing : 1 - methylmethacrylate and methacrylic acid; 2 - butylacrylate and acrylic acid; 3 - compound containing methylmethacrylate and methacrylic acid with silica flour; 4 - with glass fabric; 5 - heat-treated compound containing methylmethacrylate and methacrylic acid;

b) with butylacrylate and acrylic acid: 1 - pure compound; 2 - with silica flour; 3 - with glass fabric.

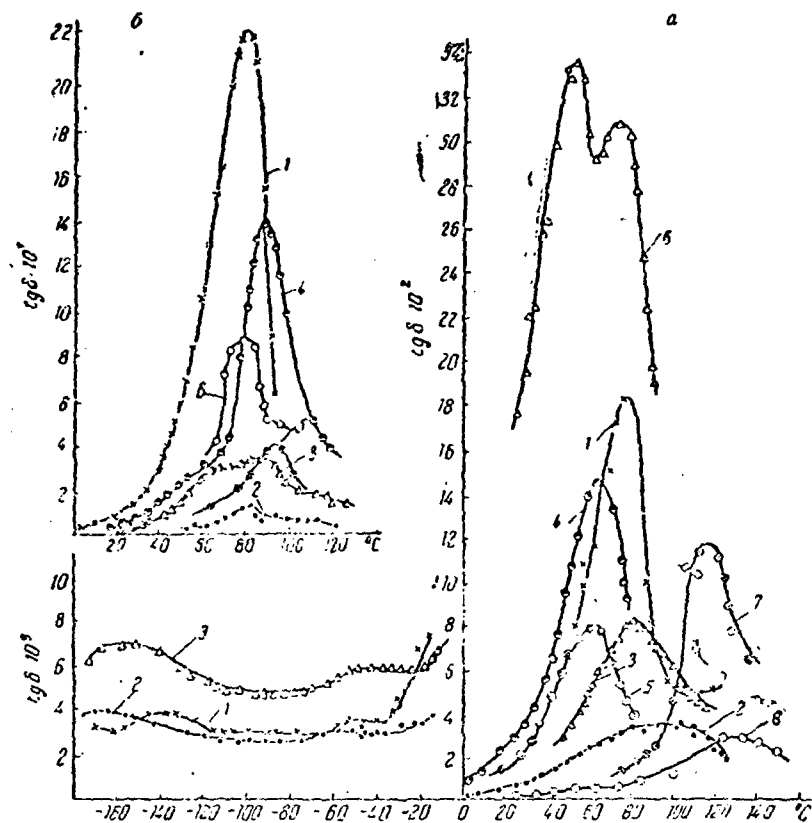


Fig 3. Temperature dependences of $\tan \delta$:

a) for compound containing methylmethacrylate and methacrylic acid: 1 - pure compound; 2 - with silica flour; 3 - with glass fabric; compounds containing methylmethacrylate and methacrylic acid (with 0.01 parts by weight of dimethylaniline): 4 - pure compound; 5 - with silica flour; 6 - with glass fabric; heat-treated compounds containing methylmethacrylate and methacrylic acid (0.05 parts by wt. of dimethylaniline): 7 - pure compound after heat treatment; 8 - compound with silica flour after heat treatment;

b) for compounds containing butylacrylate and acrylic acid: 1 - pure compound; 2 - with silica flour; 3 - with glass fabric; compounds containing methylacrylate and acrylic acid: 4 - pure compound; 5 - with silica flour; 6 - with glass fabric.

Table

Quantities of low-molecular compounds in acrylate-epoxy-styrene compounds in bulk and in the surface layers

Composition of compound	eight of low-molecular substances,	
	Vacuum treatment without heating	Vacuum treatment at 68°C for 9 hours
Methacrylic acid, methylmethacrylate, styrene, ED-6	0.92	0.43
with silica flour	0.26	0.13
with glass fabric	0.15	0.6
Acrylic acid, butylacrylate, styrene, ED-6	0.22	
with silica flour	0.15	
with glass fabric	.2	
Acrylic acid, methylacrylate, styrene, ED-6	1.5	4.82
with silica flour	0.43	1.06
with glass fabric	0.63	1.4
Methacrylic acid, methylmethacrylate, styrene, ED-6 (0.01 parts by weight of diethylaniline)	0.13	
with silica flour	0.06	
with glass fabric	0.14	

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15. Descriptors (or keywords) Acrylates, Epoxy resins, Styrene resins, Thermosetting resins, Dielectric properties, Spin lattice relaxation, Nuclear magnetic resonance, Surface properties, Fillers, Silicon dioxide, Glass fibers, Impurities, Water, Methacrylates. <div style="text-align: right;">continue on separate piece of paper if necessary</div>			
Abstract Describes an investigation of the molecular mobility of the polymer chains of acrylate-epoxy-styrene compounds and changes of molecular mobility in the boundary layers on surfaces of silica flour and glass fibre to assess their effect on the properties of the filled materials. Effects of low-molecular impurities such as water or unreacted initial monomers on the relaxation process in the surface layers were also investigated. Compounds studied were styrene: methyl-methacrylate; methacrylic acid, styrene: butacrylate; acrylic acid and styrene: methacrylate; acrylic acid.			
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